

COMMONWEALTH OF PENNSYLVANIA.

---

# Department of Agriculture.

BULLETIN No. 166.

PRELIMINARY REPORT ON

# Results of Analysis of Paris Green.

BY

F. D. FULLER, B. Sc.,

CHIEF CHEMIST OF THE DEPARTMENT.

---

*PUBLISHED BY DIRECTION OF THE SECRETARY.*

---

**HARRISBURG, PA., JUNE 1, 1908.**

---

HARRISBURG, PA.:  
HARRISBURG PUBLISHING CO., STATE PRINTER.  
1908.



# ANALYSIS OF PARIS GREEN.

## PRELIMINARY REPORT ON ITS QUALITY.

BY F. D. FULLER, B. Sc., CHIEF CHEMIST.

---

Owing to the fact that Paris green has been more commonly used in various spraying mixtures than any other arsenical poison, and that reports have come to this Department which show that serious injury was done to foliage by the use of Paris green, under certain conditions, it was thought advisable by the Legislature of 1907 to pass a law regulating the sale of this article. This act was approved by the Governor of Pennsylvania, May 29th, 1907, and became operative September 1st, of that year. The enforcement of this law was placed in the hands of the Secretary of Agriculture, who has caused samples of Paris green to be bought in the open markets of this State for examination. These samples have been submitted to chemical analysis, and, by direction of the Secretary of Agriculture, this preliminary report on the results so far secured, is made, in order to give those who may have occasion to use Paris green as an insecticide, some idea of its quality and of what may be expected of the goods now upon our markets, in so far as we are able to judge from the limited number of samples examined. The collection of samples will continue throughout the present year, and a complete report of the year's work will be issued as soon as all the work is finished.

At the present time, we have completed the examination of thirty-six samples of Paris green, representing the product of thirteen manufacturing concerns, and this work forms the basis for this publication.

### CHEMICAL COMPOSITION OF PARIS GREEN.

---

Paris green, which is known as copper aceto-arsenite, contains, when chemically pure, approximately:

Copper arsenite, .....	82 per cent.
Copper acetate, .....	18 per cent.

The active poison in Paris green is arsenic, and it is customary to refer to it as arsenious oxide, and the copper present is referred to as copper oxide. These terms are simply used for convenience in reporting the results of chemical analysis of Paris green. Therefore, using these terms, pure Paris green should contain:

Arsenious oxide, .....	58.55 per cent.
Copper oxide, .....	31.38 per cent.
Acetic acid, .....	10.07 per cent.

The composition of the commercial article, on our markets, shows a variation from these figures, which is chiefly due to a difference in manufacturing processes, and possibly to some carelessness in the manipulation.

Sodium sulphate naturally occurs in Paris green, and we also find water and sand in small quantities. Therefore, we rarely find Paris green to consist entirely of copper aceto-arsenite, but it contains this compound as its chief constituent.

Section 2 of the Paris green law states that "Paris green, when sold, offered or exposed for sale, as such, in this Commonwealth, shall comply with the following requirements: First. It shall contain arsenic, in combination with copper, equivalent to not less than fifty per centum of arsenious oxide. Second. It shall not contain arsenic, in water soluble forms, equivalent to more than three and one-half per centum of arsenious oxide, when treated for twenty-four hours with cold, distilled water, at the rate of one thousand parts by weight of water to one part by weight of Paris green."

Practically all of the injury to foliage from the use of Paris green, is caused by the presence of a considerable amount of free arsenious oxide, which is soluble in water. The presence of this water-soluble arsenic may be due to intentional addition of white arsenic, to carelessness in the manufactory, or both. The presence of white arsenic is a serious adulteration, and used only because of the fact that it is cheaper than Paris green, and its addition does not decrease the amount of total arsenious oxide. Although there may be other adulterants used in Paris green, the writer is of the opinion that adulteration with white arsenic is the most common.

## DISCUSSION OF THE RESULTS OF CHEMICAL ANALYSIS.

---

### TOTAL ARSENIOUS OXIDE.

In the thirty-six samples of Paris green examined by this Department, the amount of arsenic calculated as arsenious oxide, varied from 55.24 per cent. to 59.47 per cent., with an average of 56.82 per cent. This average is 1.73 per cent. below the equivalent of arsenious oxide in pure copper aceto-arsenite.

Judging from the total arsenious oxide present, we must infer that the quality of the Paris green on the market, is very good; but there is another constituent which we must take into consideration, and that is the amount of arsenic in water-soluble form.

### WATER SOLUBLE ARSENIC COMPOUNDS.

The amount of arsenic in water-soluble form, calculated as arsenious oxide, varied from 0.70 per cent. to 2.52 per cent., with an average of 1.48 per cent. The Paris green law requires that "it (Paris green) shall not contain arsenic in water-soluble forms, equivalent to more than three and one-half per centum of arsenious oxide, when treated for twenty-four hours with cold, distilled water, at the rate of one thousand parts by weight of water to one part by weight of Paris green." Longer extraction with water will give a solution containing a higher content of arsenic, but it seemed desirable to employ a method which would give results in conformity to those secured in actual field practice. Horticulturists very rarely allow the Paris green to remain in contact with water longer than twenty-four hours before the solution is used.

Inasmuch as Paris green containing over 3.50 per cent. of water-soluble arsenic compounds, calculated as arsenious oxide, would undoubtedly be injurious to the foliage upon which it is used, we can say that all of the different brands of Paris green from which the above samples were taken, can be used with perfect safety.

### ARSENIC IN COMBINATION WITH COPPER, CALCULATED AS ARSENIOUS OXIDE.

Paris green, to be sold according to law, must contain arsenic in combination with copper, equivalent to not less than 50 per cent. of arsenious oxide. In the samples examined, the amount of arsenic combined with copper, assuming that all of the copper is so com-

bined, varied from 51.81 per cent. to 57.68 per cent., with an average of 54.97 per cent. These results show that the samples examined were taken from packages containing Paris green of very good quality.

#### RELATION OF COPPER OXIDE TO ARSENIOUS OXIDE.

In pure copper aceto-arsenite or Paris green, there are 1.865 pounds of arsenious oxide for one pound of copper oxide. This relation is of value in showing whether Paris green has been adulterated with white arsenic. This article is used because it is cheaper than Paris green, but its presence always increases the ratio of arsenious oxide to copper oxide above 1.865.

In the thirty-six samples examined, this ratio varied from 1.88 to 2.02 and averaged 1.92. This slight variation from normal, may be due to the presence of a small amount of white arsenic or to carelessness in the manufacture; but in no case was the deviation sufficient to indicate any serious adulteration.

#### COPPER OXIDE.

The amount of copper, expressed as copper oxide, varied in the thirty-six samples from 27.78 per cent. to 30.93 per cent., with an average of 29.47 per cent., which is slightly below the amount of copper oxide in pure Paris green.

#### GENERAL CONCLUSION.

From the results obtained thus far, we can state that the Paris green market of Pennsylvania seems to be in a very satisfactory condition, and this article may be used with a fair degree of safety at the present time, unless a more extended examination reveals facts which will prove the contrary.

COMMONWEALTH OF PENNSYLVANIA.

---

## Department of Agriculture.

BULLETIN No. 166.

PRELIMINARY REPORT ON

# Results of Analysis of Paris Green.

BY

F. D. FULLER, B. Sc.,

CHIEF CHEMIST OF THE DEPARTMENT.

---

*PUBLISHED BY DIRECTION OF THE SECRETARY.*

---

HARRISBURG, PA., JUNE 1, 1908.

---

HARRISBURG, PA.:  
HARRISBURG PUBLISHING CO., STATE PRINTER.  
1908.

